The Convection Dispersion Equation-
not the Question, the Answer!

Anion and Cation Transport through Undisturbed Soil Columns during Unsaturated Flow

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Abstract

Prediction of solute movement through the unsaturated zone is important in determining the risk of groundwater contamination from both "natural" and surface applied chemicals. In order to understand better the mechanisms controlling this water-borne transport, unsaturated leaching experiments were carried out on undisturbed soil columns, about 3 litres in volume, for two contrasting soils. One was the weakly-structured Manawatu fine sandy loam, and the other the well-aggregated Ramiha silt loam. Anion transport was satisfactorily described using the convection dispersion equation (CDE), provided that anion exclusion for the Manawatu soil, and adsorption for the Ramiha soil were taken into account. At water flux densities of about 3 mm h^{-1}, a dispersivity of about 40 mm was obtained for the Manawatu soil, and a dispersivity of about 15 mm for the Ramiha soil. The difference was probably due to the contrasting structures of the two soils. Increasing the water flux density in the Manawatu soil to about 13 mm h^{-1} resulted in a slightly higher dispersivity of about 60 mm.

Flow interruption resulted in a subsequent drop in the effluent concentration for the Manawatu soil but not in the Ramiha soil. This suggests that the lag time for transverse molecular diffusion from "mobile" to "immobile" water domains was important in the Manawatu soil, but not in the Ramiha soil.

In both soils cation transport was described satisfactorily with the CDE in conjunction with cation exchange theory, providing that only 80% of the cations replaced by 1 *M* ammonium acetate were assumed to be involved in exchange reactions.

Column leaching experiments were also carried out using a rainfall simulator and larger columns of about 22 litres of the Manawatu soil with a short pasture on top. Solid chemical was applied to both a dry and a wet soil surface. Neither the pasture nor the initial water content had a significant effect on solute movement. Slightly higher dispersivities of about 70 mm were found.

Time Domain Reflectometry (TDR) was found to be valuable for monitoring solute transport in a repacked soil under transient water flow conditions. But in undisturbed soils TDR only proved to be accurate under steady-state water flow when absolute values of solute concentration were not sought.

The CDE was thus found to satisfactorily answer the question of how to describe transport of non-reactive and reactive solutes under bare soil and under short pasture. This applied during both steady-flow and transient wetting.

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List of Symbols

Roman Symbols

a	empirical constant	[m^3 kg^{-1}]
a_1 , a_2	variables in computer program	-
b	empirical constant	-
b_1, b_2	variables in computer program	[kg or mol m^{-3}]
c	propagation of an electromagnetic wave in free space	[m s^{-1}]
c_1, c_2	variables in computer program	[(mol $m^{-3})^2$]
c_3	empirical constant	-
d	empirical constant	-
f	fraction of exchange sites in immobile water domain	-
f_c	temperature correction coefficient	-
$f_t(Q)$	solute probability function of cumulative infiltration	[m^{-1}]
$f_t(t)$	solute travel-time probability function	[s^{-1}]
g	solute life-time probability function	[s^{-1}]
h_o	pressure head	[m]
l	column length or calibration length	[m]
l_a	apparent TDR probe length	[m]
l_t	TDR probe length	[m]
n	constant in Eq. 2.22 and Eq. 2.40	-
q_d	diffusional flux exchange between mobile and immobile water	[kg or mol m^{-2} s^{-1}]
q_i	solute flux in immobile phase	[kg or mol m^{-2} s^{-1}]
q_m	solute flux in mobile phase	[kg or mol m^{-2} s^{-1}]
q_w	water flux density	[m s^{-1}]
q_s	solute flux density	[kg or mol m^{-2} s^{-1}]
r	voltage reflection coefficient	-
t	time	[s]
t'	input time	[s]
v	pore water velocity	[m s^{-1}]

v_p	relative velocity setting on TDR instrument	-
v_e	propagation velocity of an electromagnetic pulse	[m s^{-1}]
x	variable in computer program	[kg or mol m^{-3}]
y	variable in computer program	[kg or mol m^{-3}]
z	depth	[m]

A_s	cross-sectional area	[m^2]
A	ion species	-
B	ion species	-
C	concentration in soil solution	[kg or mol m^{-3}]
$C_a(z)$	depths-dependent initial soil solution concentration	[kg or mol m^{-3}]
C_{ai}	total initial anion concentration	[kg or mol m^{-3}]
C_A	concentration of cation species A in soil solution	[kg or mol m^{-3}]
C_B	concentration of cation species A in soil solution	[kg or mol m^{-3}]
C_f	flux-averaged solute concentration	[kg or mol m^{-3}]
C_i	resident soil solution concentration in immobile phase	[kg or mol m^{-3}]
C_m	resident soil solution concentration in mobile phase	[kg or mol m^{-3}]
$C_o(t)$	time-dependent input solution concentration	[kg or mol m^{-3}]
C_r	resident soil solution concentration	[kg or mol m^{-3}]
C_s	soil solution concentration of ion species s	[kg or mol m^{-3}]
C_T	total cation concentration in soil solution	[kg or mol m^{-3}]
C_1	constant concentration	[kg or mol m^{-3}]
D_s	hydrodynamic dispersion coefficient	[m^2 s^{-1}]
D_i	diffusion coefficient in soil	[m^2 s^{-1}]
D_m	dispersion coefficient in mobile phase	[m^2 s^{-1}]
D_w	soil water diffusivity	[m^2 s^{-1}]
D_o	diffusion coefficient in water	[m^2 s^{-1}]
F_{in}	solute mass flux entering soil volume	[kg or mol s^{-1}]
F_{ex}	solute mass flux leaving soil volume	[kg or mol s^{-1}]
I	ionic strength	-
J_c	convective solute flux in mobile water	[kg or mol m^{-2} s^{-1}]

J_{disp}	dispersive solute flux in mobile water	[kg or mol m^{-2} s^{-1}]
J_E	diffusional flux exchange between mobile and immobile water	[kg or mol m^{-2} s^{-1}]
J_L	longitudinal diffusional flux	[kg or mol m^{-2} s^{-1}]
K_{A-B}	selectivity coefficient for cation species A and B	-
K_{M-D}	selectivity coefficient in Gapon equation	[(mol $kg^{-3})^{1/2}$]
K_d	distribution coefficient	[m^3 kg^{-1}]
K_G	geometric constant of TDR probe	[m^{-1}]
K_s	saturated hydraulic conductivity	[m s^{-1}]
K_w	hydraulic conductivity	[m s^{-1}]
L_D	diffusion/dispersion length parameter	[m]
L_{diff}	diffusion length parameter	[m]
L_{dis}	dispersion length parameter	[m]
L_{mim}	mobile/immobile exchange length parameter	[m]
M_o	pulse of solute applied to soil surface	[kg or mol m^{-2}]
M	total solute concentration	[kg or mol m^{-3}]
M_i	solute mass in immobile phase	[kg or mol m^{-3}]
M_m	solute mass in mobile phase	[kg or mol m^{-3}]
P	Pèclet number	-
R	retardation factor	-
R_C	radius of cylinders of porous soil	[m]
R_H	radius of cylindrical macropores	[m]
R_S	radius of spheres	[m]
Q	cumulative drainage or infiltration	[m]
R	solute retardation factor	-
S	sorptivity	[m $s^{-1/2}$]
S_s	amount of solute adsorbed	[kg or mol kg^{-1}]
T	travel time of electromagnetic pulse	[s]
V_o	zero reference voltage	[V]
V_f	final reflected voltage at very long time	[V]
V_i	voltage of incident step	[V]
V_r	voltage after reflection from probe end	[V]

X_A	charge concentration of cation species A on exchanger	[mol_c kg^{-1}]
X_{CEC}	charge concentration of adsorbed cations	[mol_c kg^{-1}]
Z_o	characteristic impedance	[Ω]
Z_L	impedance of TDR probe	[Ω]

Greek Letters

α	mass transfer coefficient	[s^{-1}]
β	constant	-
δ	Dirac delta function	-
ε	dielectric constant	-
γ	constant	-
λ	dispersivity	[m]
λ_{eff}	effective dispersivity	[m]
λ_m	dispersivity in mobile water	[m]
λ_{meff}	effective dispersivity in mobile phase	[m]
λ_{num}	numerical dispersivity	[m]
μ_l	mean of the lognormal distribution	[s]
ρ_b	soil bulk density	[kg m^{-3}]
σ	bulk soil electrical conductivity	[S m^{-1}]
σ_l	variance of the lognormal distribution	[s]
σ_s	surface conductance	[S m^{-1}]
σ_w	pore water electrical conductivity	[S m^{-1}]
τ	tortuosity factor	-
θ	volumetric water content	[m^3 m^{-3}]
θ_a	residual water content	[m^3 m^{-3}]
θ_i	immobile water fraction	[m^3 m^{-3}]
θ_m	mobile or effective water fraction	[m^3 m^{-3}]
θ_n	initial water content	[m^3 m^{-3}]

θ_s	saturated water content	[$m^3 m^{-3}$]
θ_x	excluded water fraction	[$m^3 m^{-3}$]
ω	attenuation coefficient	-

Subscripts

n	depth position
j	time index
Ca	calcium
D	divalent
K	potassium
Na	sodium
M	monovalent
Mg	magnesium
CM	calcium plus magnesium

Abbreviations

BTC	breakthrough curve
CDE	convection dispersion equation
CEC	cation exchange capacity
CLT	convective lognormal transfer function
E_l	expected mean travel time at reference depth l
E_z	expected mean travel time at depth z
MIM	mobile/immobile concept
pdf	probability density function
REV	representative elementary volume
REA	representative elementary area
TDR	time domain reflectometry
Var_l	variance at reference depth l
Var_z	variance at depth z